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DEVELOPMENT OF AN EXTERNAL CERAMIC
INSULATION FOR THE SPACE SHUTTLE ORBITER

Part 3 — Development of Stabilized Aluminum Phosphate Fibers

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Philadelphia, Pa.

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Prepared
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

October 1973

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FOREWORD

This report was prepared by the Re-Entry and Environmental Systems Division (RES-D) of the General Electric Company, Philadelphia, Pennsylvania under NASA Contract No. NAS 1-10533. The work was administered under the direction of the Langley Research Center's Thermal Protection Materials Branch with Mr. A. J. Chapman, III acting as Contract Monitor.

This report covers the work conducted from April 6 through August 6, 1973 at the RES-D's Advanced Materials Development Laboratory under the management of Dr. R. A. Tanzilli. The authors of the report acknowledge the technical support of Dr. S. Musikant, Manager, Metallurgy and Ceramics Laboratory and Professor Floyd Hummel of the Pennsylvania State University who acted as program consultants.

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SECTION 1

INTRODUCTION

1.1 PROGRAM GOAL

The studies of reusable surface insulation materials during earlier phases of this contract (Ref. 1, 2) have shown the need for a ceramic fiber which would be more resistant to thermal shock as well as being highly refractory. To have these properties, a ceramic material should have a low thermal expansion and a stable phase structure throughout the temperature range of use. A reusable surface insulation fabricated from such a fiber would offer a significantly improved heat shield for the Space Shuttle

General Electric Co. - sponsored research (Glass Research Lab) at the Pennsylvania State University under the direction of Professor Floyd A. Hummel indicated that the development of a stabilized, high-cristobalite, aluminum orthophosphate (AlPO_4) fiber would possess these desired qualities. The research program which was conducted to develop this material is described in the following subsections.

1.2 PREVIOUS WORK

1.2.1 SIMILARITY OF AlPO_4 and SiO_2

In 1949, Hummel (Ref. 3) clearly demonstrated the isostructural similarities of AlPO_4 and SiO_2 . In particular, his thermal expansion data showed that the high-cristobalite (β) forms of AlPO_4 and SiO_2 are thermally stable between 573K (572° F) and 1973K (3092° F) and that each has a low coefficient of thermal expansion over the 1400K temperature interval (approaching that of amorphous silica).

The deterrent to the use of either of these materials in the high-cristobalite form is the catastrophic volume change which takes place during the high - to - low - cristobalite ($\beta \rightleftharpoons \alpha$) transition in the temperature range between 473-573K. Figure 1 illustrates the discontinuity in thermal expansion associated with this transition for both cristobalite modifications.

If one could stabilize, however, the high-cristobalite phase for either system, a unique thermal - shock resistant ceramic possessing the ideal property combinations of high refractoriness and low thermal expansion would result. For this program stabilization of the high-cristobalite phase of AlPO_4 was chosen (as depicted in Figure 1) since this system presented many more opportunities for chemical stabilization than SiO_2 .

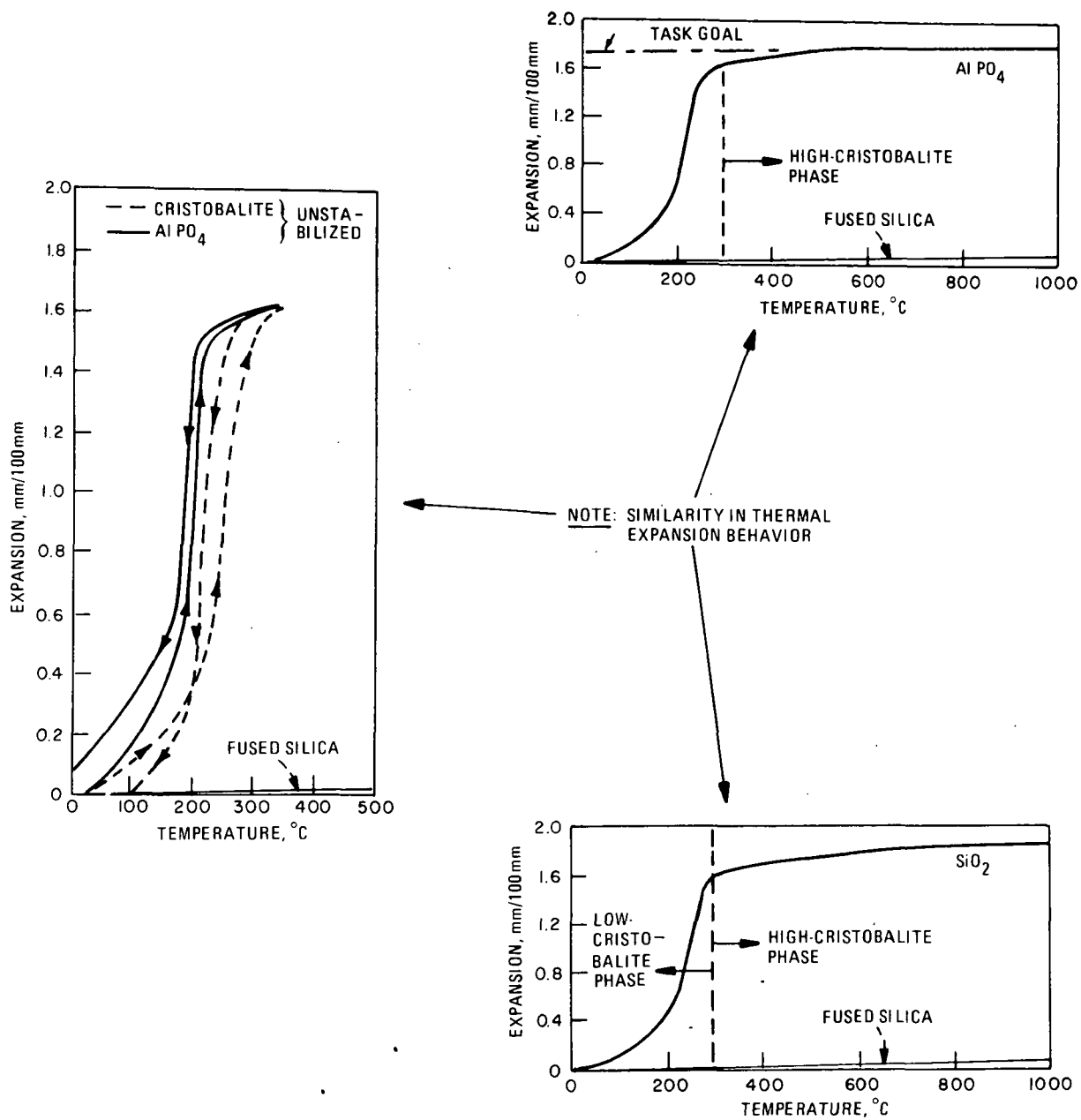


Figure 1. Comparison of thermal expansion behavior of low - and high-cristobalite phases of AlPO_4 and SiO_2 (Ref. 3)

1.2.2 PRECEDENT FOR PHASE STABILIZATION

The feasibility of achieving chemical stabilization of a ceramic phase is probably best illustrated by zirconia. By adding substitutional quantities of MgO, CaO, Y_2O_3 or other oxides to ZrO_2 , it can be maintained in a cubic form from room temperature to its melting point, thus, eliminating the catastrophic volume change associated with the low temperature transition to the monoclinic form. During an earlier phase of this program (Ref. 1), an yttria - stabilized zirconia fiber produced synthetically by the Union Carbide Corp. (Zircar [®]) was evaluated for RSI applications up to 2035K (3200° F).

Numerous examples of phase stabilization by substitutional or interstitial alloying exist also in the metallurgy field, most noteworthy being the stabilization of the austenite phase in steel.

1.2.3 STABILIZER SELECTION

The elimination of an undesirable phase transformation may be achieved by the addition of an appropriate element which enters into solid solution with the phase to be stabilized. As mentioned previously, aluminum orthophosphate ($AlPO_4$) offered greater latitude than silica (SiO_2) for achieving stabilization because substitutions of two different valences would be possible, i. e. Al^{3+} or P^{5+} .

Previous research had indicated that B^{3+} , Sc^{3+} and Ga^{3+} substitutions would form solid solutions with $AlPO_4$. In addition, a literature review indicated that Fe^{3+} and Cr^{3+} also entered into solid solution with $AlPO_4$ (Ref. 4). No data was found for P^{5+} site substitutions. In addition to single replacement of Al^{3+} or P^{5+} , simple substitutions could also be made simultaneously on the 3^+ and 5^+ lattice sites. Other possible substitutions could involve coupling on either the Al^{3+} site, the P^{5+} site, or on both sites simultaneously. For example, Mg^{2+} and Si^{4+} cations might be substituted for 2 Al^{3+} . The major requirement for each of these approaches involves the maintenance of charge-balance.

Structural considerations, such as, ionic radii, also enter into the criteria for successful solid solution formation, however, the theory for such criteria is incomplete at the present time. The basic approach taken during this initial feasibility study was to generally limit substitutions to single site replacements at the Al^{3+} or P^{5+} sites. (See Section 2.3)

1.2.4 SOLID SOLUTION FORMATION

Since the end-item of this research was the formation of small-diameter fibers for possible utilization in an RSI heat shield, the possible solid-solution formation techniques were limited. The salt-decomposition method (originally developed by

Blaze at Babcock and Wilcox Co. - Ref. 5, 6, 7) was selected at program outset because of its already demonstrated success in making small diameter mullite and alumina fibers. The process involves the utilization of a viscous precursor salt solution whose mean composition yields the desired chemical formulation after thermal decomposition and sintering. Fiber formation occurs at or near room temperature by adjustment of the surface tension and viscosity of the precursor salt solution. (See Section 2.2).

SECTION 2

EXPERIMENTAL PROCEDURE AND RESULTS

2.1 INTRODUCTION

As mentioned earlier, solid-solution formation was accomplished using the salt-decomposition method which provided rapid homogenization due to the high degree of constituent mixing during initial consolidation and which was also readily adaptable to fiber formation. Solid solutions could also be formed by the sintering and diffusion of constituent oxide and phosphate powders. However, this approach was not as readily adaptable to fiberization as was the salt decomposition method and therefore was not used during this study.

X-ray diffraction was used as the primary means for determining the crystal structure of modified AlPO_4 solid solutions. Stabilized high-cristabalite AlPO_4 solid-solutions were then evaluated (preferably in an RSI configuration) to determine their thermal expansion characteristics. In addition, microstructural features such as surface topography, fiber-diameter distribution and grain size were determined using optical and scanning electron microscopy techniques. Finally, thermal aging studies were conducted on promising compositions to simulate ultimate application.

Descriptions of the fiber-formation process, stabilization-formulation selection, and subsequent fiber characterization are given below.

2.2 FIBER FORMATION PROCESS

A flow chart describing the process for making fibers is shown in Figure 2. A viscous solution is made by dissolving aluminum metal in a solution of phosphoric acid and aluminum chloride. Various other compounds are then added to the solution in the form of soluble metallic salts. When the aluminum and salts are dissolved, the solution is filtered and boiled down to a solids content of about 42 - 45%. Acetic acid or isopropyl alcohol is added to the solution in quantities of 0 - 5% by volume to reduce the surface tension. Figure 3 shows the solution as it is ready for spinning.

The fiber spinning apparatus consists of a 15.24 cm diameter drum with 0.159 cm holes drilled in the sides. This drum is filled with the viscous solution and spun at about 3600 rpm. Centrifugal force throws the solution out through the holes and forms the fibers. A fan is placed behind the spinning drum to blow the fibers onto a wire cage where they can be dried and peeled off in a paper-like sheet. Figures 4 and 5 show the apparatus making the fibers and the paper as it is peeled off.

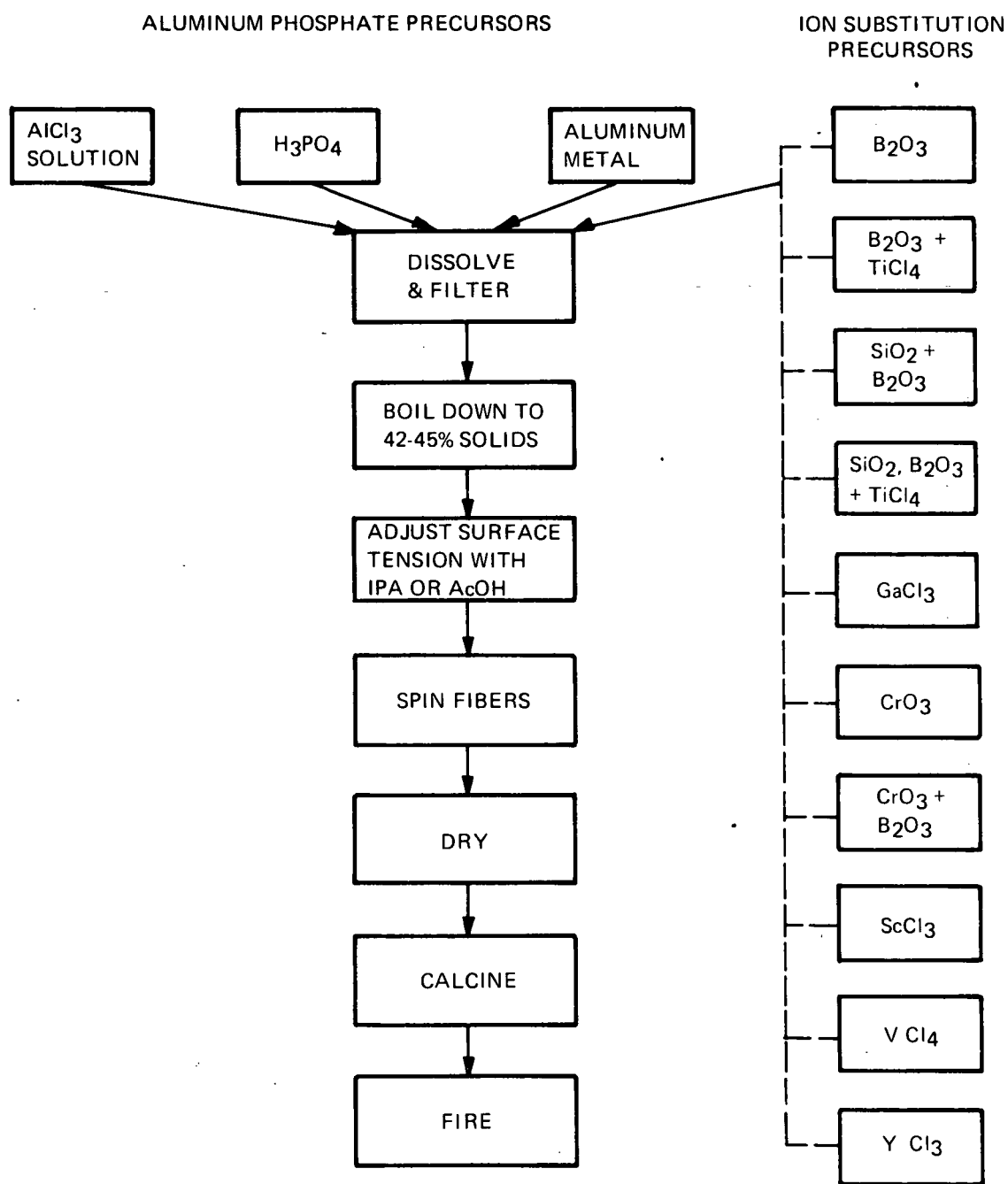


Figure 2. Process flow chart

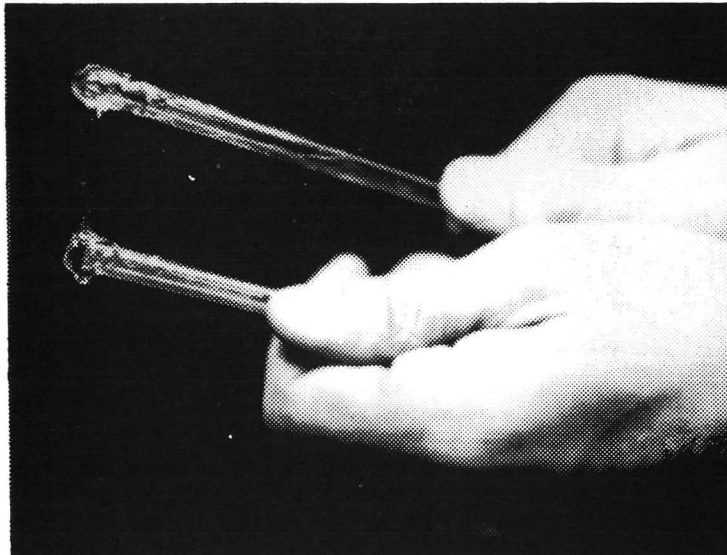


Figure 3. Viscous solution ready for fiberizing

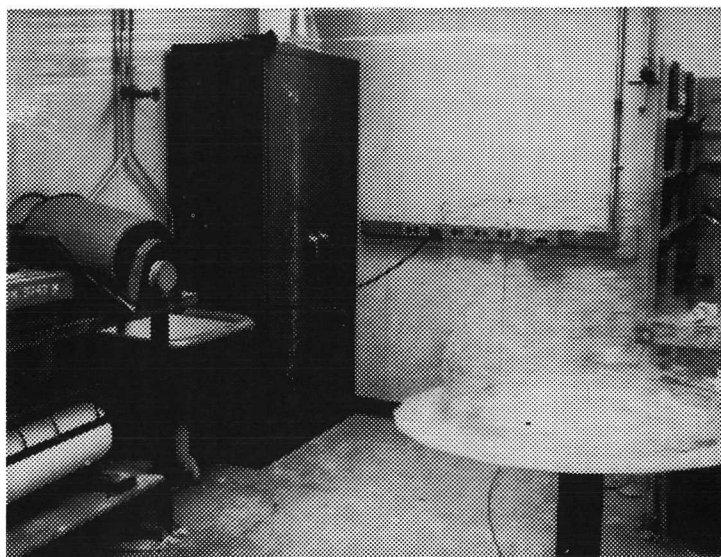


Figure 4. Fiberizing apparatus



Figure 5. Fibers being removed from the wire cage

The fibers are carefully dried at 394 K (250° F) inside a closed bell jar. The bell jar, shown in Figure 6, prevents the scattering of the fibers due to air currents in the drier and also allows a more gradual drying.

The dried fibers are then calcined at 978 to 1033 K (1300 to 1400° F) for one to sixteen hours to decompose the salts and break down the hydrogen bonding in the fibers. This yields a fiber which is mostly amorphous but which also contains small amounts of quartz, tridymite and cristobalite. The fibers are not soluble in water after this treatment.

2.3 FIBER FORMULATIONS

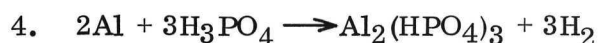
2.3.1 PRECURSOR FORMULATIONS

Aluminum phosphate is formed by dissolving aluminum metal in a mixture of aluminum chloride solution and phosphoric acid. This reaction yields a sticky mass of various aluminum hydrogen phosphates and colloidal aluminum hydrate. The chemical reactions taking place are approximately:

1. $2\text{Al} + \text{AlCl}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + \text{AlCl}_3 + 6\text{HCl}$
2. $\text{Al} + 2\text{H}_3\text{PO}_4 \rightarrow \text{AlH}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O} + 1-1/2 \text{H}_2$



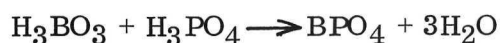
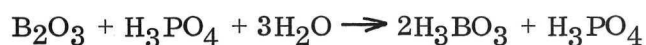
Figure 6. Bell jar arrangement for drying fibers



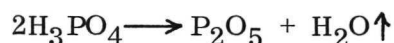
The reaction products are all hydrated forms of alumina and aluminum phosphate which upon heating decompose to yield aluminum orthophosphate (AlPO_4).

To produce a material with a cation substituted for the Al^{3+} ion, a soluble salt containing the desired cation is dissolved along with the aluminum phosphate precursors. If, for instance, a soluble metal chloride is included with an excess of phosphoric acid, the two materials will react upon heating to yield a phosphate, i.e., $\text{RCl}_3 + \text{H}_3\text{PO}_4 \longrightarrow \text{RPO}_4 + 3\text{HCl} \uparrow$.

In the case of a soluble oxide such as boric oxide (B_2O_3) the reaction is much the same, i.e.,



Batch calculations were made based on the molar content of the precursor materials. These molar contents are shown in Table 1. To obtain an AlPO_4 lattice with a 10% substitution of B^{3+} for Al^{3+} a solution was made up with 2.25 moles of Al^{3+} ion from the AlCl_3 and Al metal precursors and .25 moles of B^{3+} ion using boric oxide (B_2O_3) as a precursor. To balance the formula 2.5 moles of PO_4^{3-} ion should be added in the form of concentrated phosphoric acid (H_3PO_4). It was found that a slight excess of phosphoric acid produced a somewhat better fiberizing solution so approximately 0.1 moles excess PO_4^{3-} ion was added to the solution. The extra phosphoric acid was later removed during the drying-calcining operations by the following reaction:



The precursor formulations which were used to spin various fiber compositions are shown in Table 2 along with the expected composition after the salts are decomposed.

Table 1. Stoichiometric Equivalents

<u>ION</u>	<u>Source</u>	<u>Molar Content</u>
Al^{3+}	Aluminum Metal	3.7×10^{-2} moles/g
Al^{3+}	Aluminum Chloride Solution 32° Be	2.67×10^{-3} moles/ml
PO_4^{3-}	Phosphoric Acid (H_3PO_4)	1.61×10^{-2} moles/ml
B^{3+}	Boric Oxide (B_2O_3)	2.87×10^{-2} moles/g
Ti^{4+}	Titanium Tetrachloride (TiCl_4)	9.1×10^{-3} moles/ml
Si^{4+}	Ludox AS	5×10^{-3} moles/ml
Ga^{3+}	Gallium Chloride (GaCl_3)	1.4×10^{-2} moles/ml
Cr^{3+}	Chromic Oxide (CrO_3)	2.6×10^{-2} moles/g
Sc^{3+}	Scandium Trichloride (ScCl_3)	2.6×10^{-3} moles/g
V^{3+}	Vanadium Tetrachloride (VCl_4)	9.42×10^{-3} moles/ml

Table 2. Precursor Solutions

Composition of Precursor

Compos. No.	Desired Molar Compos. of Decomposed Salts	Dist. Water	Alum Chl. Solution	Aluminum Metal	Phos. Acid (H_3PO_4)	Boric Oxide (B_2O_3)	Other Additives
1	$AlPO_4$	300 ml	332 ml	37.5 gm	145 ml	--	--
2	94% $AlPO_4$ 6% BPO_4	300 ml	332 ml	37.5 gm	162 ml	5.4 gm	--
3	90% $AlPO_4$ 10% BPO_4	300 ml	332 ml	37.5 gm	162 ml	9 gm	--
4	89% $AlPO_4$ 10% BPO_4 1% TiO_2	300 ml	332 ml	37.5 gm	162 ml	9 gm	2 ml Titanium Tetrachloride ($TiCl_4$)
5	60% $AlPO_4$ 30% SiO_2 10% BPO_4	330 ml	221 ml	25 gm	108 ml	9 gm	150 ml Ludox AS Colloid Silica
6	89% $AlPO_4$ 4% SiO_2 5% BPO_4 2% $TiCl_4$	300 ml	332 ml	37.5 gm	162 ml	4.5 gm	20 ml Ludox, 4 ml Titanium Tetrachloride
7	90% $AlPO_4$ 10% $GaPO_4$	300 ml	332 ml	37.5 gm	162 ml	0	9 ml Molten Gallium Trichloride ($GaCl_3$)
8	90% $AlPO_4$ 10% $CrPO_4$	300 ml	332 ml	37.5 gm	162 ml	0	9.6 gm Chromic Oxide (CrO_3)
9	90% $AlPO_4$ 5% BPO_4 5% $CrPO_4$	300 ml	332 ml	37.5 gm	162 ml	4.5 gm	4.8 g Chromic Oxide (CrO_3)
10	90% $AlPO_4$ 10% $ScPO_4$	80 ml	86.7 ml	9.8 gm	42 ml	0	10 gm Scandium Trichloride ($ScCl_3$)
11	90% $AlPO_4$ 10% VPO_4	300 ml	332 ml	37.5 gm	162 ml	0	27.5 ml Vanadium Tetrachloride (VCl_4)
12	90% $AlPO_4$ 10% YPO_4	300 ml	332 ml	37.5 gm	162 ml	0	25 gm Yttrium Chloride (YCl_3)

2.3.2 DRYING AND FIRING

The initial attempts at drying the fibers displayed some difficulty as the fibers would tend to liquefy and shrink if heated too fast. A careful drying procedure had to be established in which the fibers were allowed to air dry at room temperature for several days before they were placed in a drying oven. This initial air dry was later accelerated by warming the fibers to 310–322 K for four (4) hours using radiant lamps as a heat source. Once the initial drying was completed the fibers could then be dried at 394 K without serious shrinkage. A drying time of about two hours at this temperature produced a fiber which was dimensionally stable.

Various heat treatments were tried ranging from 478 K (400° F) up to 1644 K (2500° F). An understanding of the specific chemical changes expected can be gained by studying the equilibrium reactions shown in Figure 7. This chart shows the expected reactions for pure AlPO_4 . It was assumed that the various additions to the AlPO_4 would act as a flux to cause the reaction to take place at a lower temperature than that shown. The initial heat treatments yielded various amounts of quartz (berlinite), tridymite, alpha-cristobalite, and some beta-cristobalite. A general trend was observed that above 1478 K (2200° F) the amount of beta-cristobalite seemed to increase for a short amount of time and then reverted to alpha-cristobalite. It was hypothesized that either the substitutional ions or the phosphate ions were lost by evaporation before complete solid solution could be accomplished.

In an effort to control the evaporation of volatiles during firing several methods of controlled atmosphere firing were attempted. A sealed vessel was first employed so that any volatile constituents would reach an equilibrium state in the closed system. Since boric oxide and phosphorous pentoxide (which are both produced during salt decomposition) are both volatile, open containers of these materials were placed inside some of the sealed vessels during firing to create a saturated atmosphere. In all cases the fibers still produced only small amounts of beta-cristobalite and a large amount of alpha-cristobalite, quartz, and tridymite.

A vessel with the configuration shown in Figure 8 was then prepared and boron phosphate (BPO_4) was placed in the vessel with the fibers. This material decomposes at elevated temperatures (well above the vaporization temperature of P_2O_5) releasing B_2O_3 and P_2O_5 vapors. It was reasoned that if P_2O_5 or B_2O_3 evaporation was somehow affecting the equilibrium of the fibers then this controlled atmosphere saturation developed at elevated temperatures would minimize such evaporation. It was found that firing the 90% AlPO_4 - 10% BPO_4 in this manner did produce a stable beta-cristobalite material.

The results of x-ray diffraction tests of various AlPO_4 solid solutions are shown in Table 3. The results indicate the probable equilibrium state of the material since all materials were soaked at least 16 hours and usually 64 hours before XRD examination. These results show that the high-cristobalite form of AlPO_4 can be stabilized by additions of BPO_4 , BPO_4 and TiO_2 , SiO_2 and BPO_4 , and ScPO_4 (compositions: 3, 4, 5, and 10, Table 3).

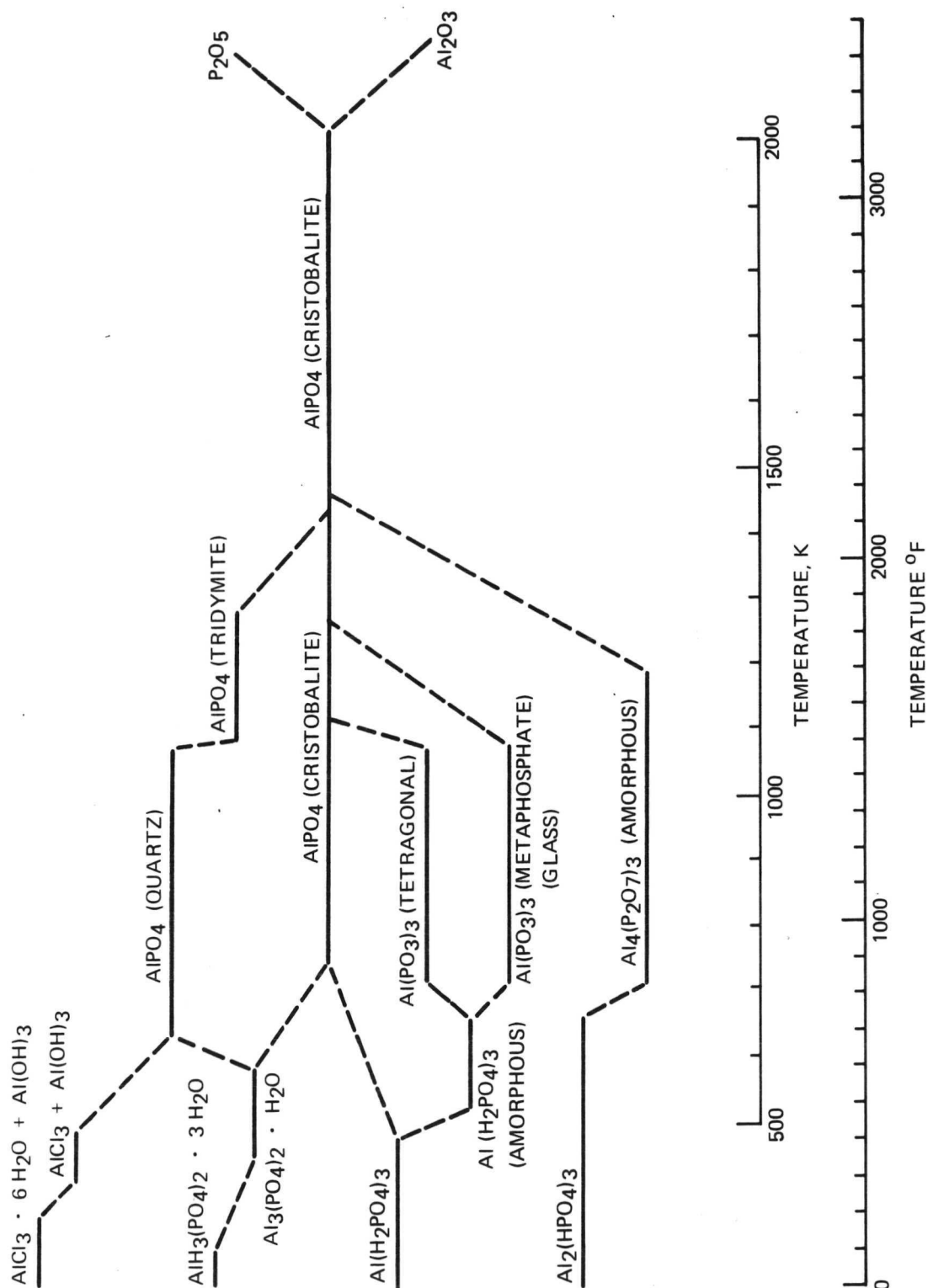


Figure 7. Aluminum phosphate reactions

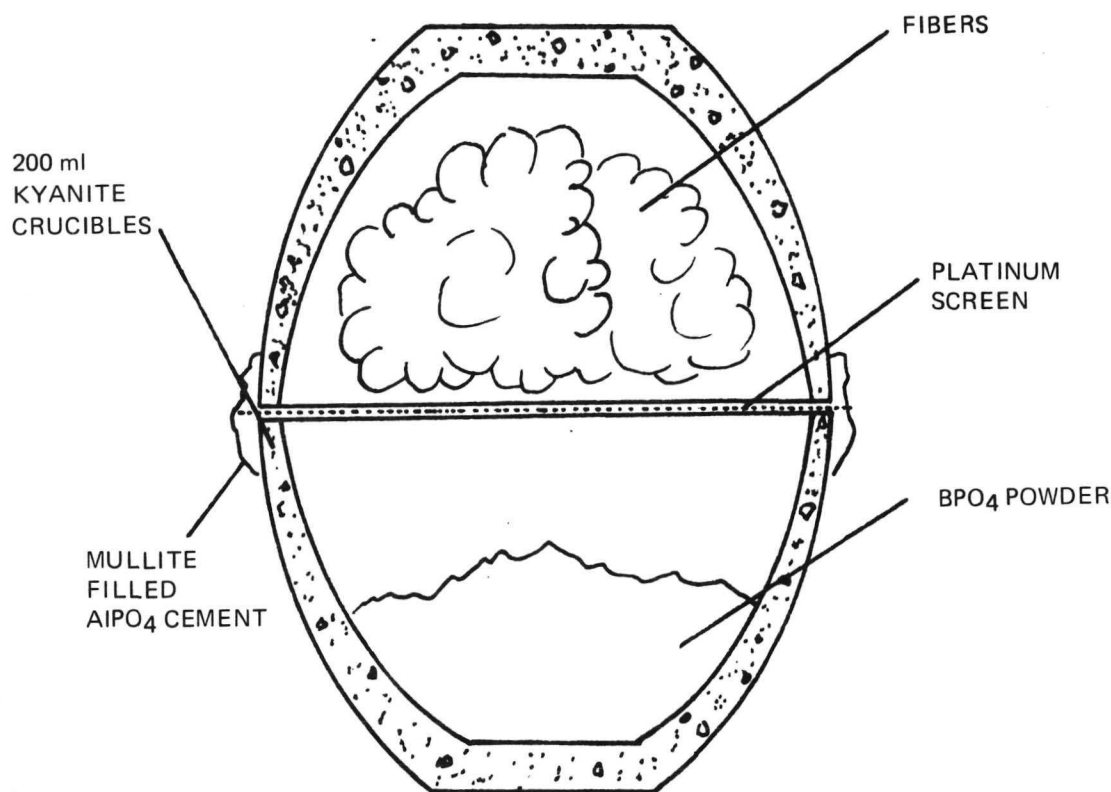


Figure 8. Firing vessel for controlling calcining atmosphere

2.4 FIBER CHARACTERIZATION

2.4.1 X-RAY DIFFRACTION

The high (β) and low (α) cristobalite phases of AlPO_4 are geometrically similar to those of SiO_2 (although not identical). Ordering of Al^{3+} and P^{5+} atoms on the Si^{4+} sites leads to an orthorhombic, pseudo-cubic supercell in the case of the low-cristobalite phase, and to a tetragonal subcell in the case of the high-cristobalite phase (Reference 8).

Horn (Reference 9) has shown that the two major reflections (i.e., 101 and 112) for the high (β) cristobalite form of AlPO_4 occur at the following d-spacing: 4.04 Å and 2.49 Å (which correspond to $2\theta = 21.8$ and 35.9° for $\text{CuK}\alpha$). By contrast the presence of the low (α) cristobalite phase is characterized by the presence of two additional relatively strong reflections at $2\theta = 28$ and 31° (for $\text{CuK}\alpha$ radiation). Figures 9 and 10 show these typical low-angle reflections for both a stabilized high-cristobalite form of AlPO_4 (boron substitution) and the unstabilized low-cristobalite form, respectively. The achievement of the former diffraction pattern (Figure 9) after fiber synthesis was the criterion used for assessing successful stabilization. The x-ray diffraction data shown in Table 3 was arrived at using the previously described criterion.

Table 3. Effect of Additives on Aluminum Phosphate Solid Solutions

Composition Number	Stabilizing Dopant(s)	Average Ionic Radius of Dopants(A)	Heat Treatment Temperatures						Remarks
			477K (In Steam)	1033K (In Air)	1255K (In Air)	1477K (In Air)	1561K (In BP0 ₄)	1644K (In BP0 ₄)	
1	None	-	B, M, V	B, V	B, α C	60% α C	100% α C	100% α C	
2	6% BP0 ₄	0.23	B, M, V	B, V	B, α C	60% α C	100% α C	100% α C	
3	10% BP0 ₄	0.23	B, M, V	B, V	B, β C	*70% β C	* 80% β C	100% α C	Forms stable β - cristobalite after 64 hours at 1561K
4	10% BP0 ₄ 1% TiO ₂	0.28	-	T, V	β C, V	80% β C	85% β C	100% α C	Forms stable β - cristobalite after 16 hours at 1477K
5	30% SiO ₂ 10% BP0 ₄	0.37	-	B, β C, V	B, β C, V	*50% β C	Melts	-	Fibers shrink rapidly above 1255K
6	4% SiO ₂ , 5% BP0 ₄ , 2% TiO ₂	0.43	-	T, β C	T, β C	T, α C	-	-	
7	10% GaP0 ₄	0.62	-	-	-	α C	α C	Melts	
8	10% CrP0 ₄	0.63	V	V	B, V	B, α C	B, α C	-	
9	5% CrP0 ₄ 5% BP0 ₄	0.43	-	B, V	B, V	B, α C	B, α C		
10	10% ScP0 ₄	0.73	-	-	-	60% β C	70% β C	70% β C (**)	Only form of β - cristobalite stable at 1644K found in this study
11	10% VP0 ₄	0.74	-	-	-	80% α C	Melts	-	
12	10% YP0 ₄	0.89				α C	α C	α C	

KEY: B Berlinite (Quartz form - hexagonal)

M Metaphosphate phases i. e. : Al(H₂P0₄)₃, Al₂(HP0₄)₃

V Vitreous (amorphous)

α C alpha or low cristobalite

β C beta or high cristobalite

T tridymite (tetragonal)

NOTE: The data shown indicates the composition after 16 hours at temperature unless preceded by a *, which indicates 64 hours at temperature.

**Percentage remainders represent an amorphous component.

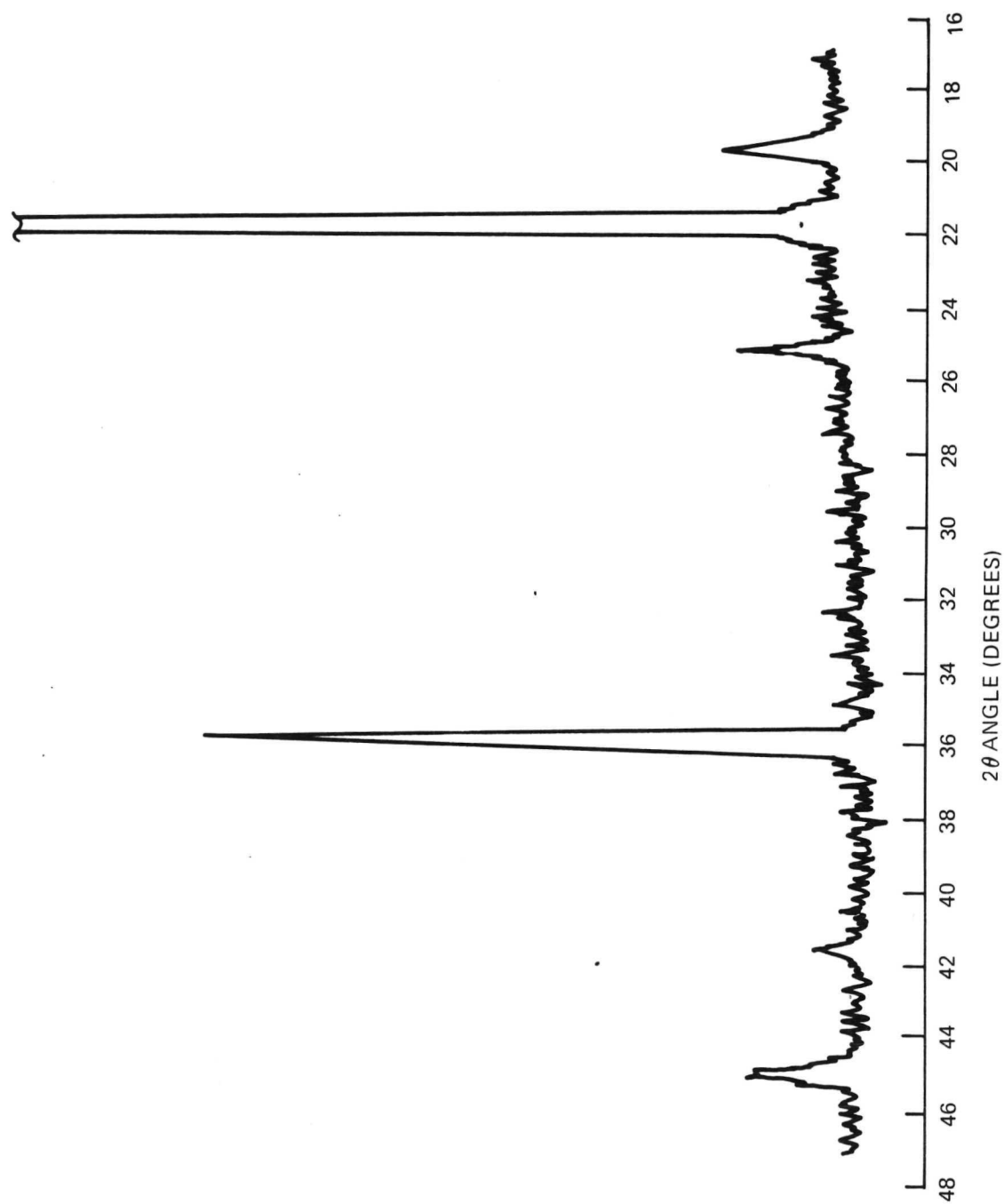


Figure 9. X-ray diffraction pattern for the stabilized high (β) cristobalite phase of AlPO_4 . (Radiation: CuK_α)

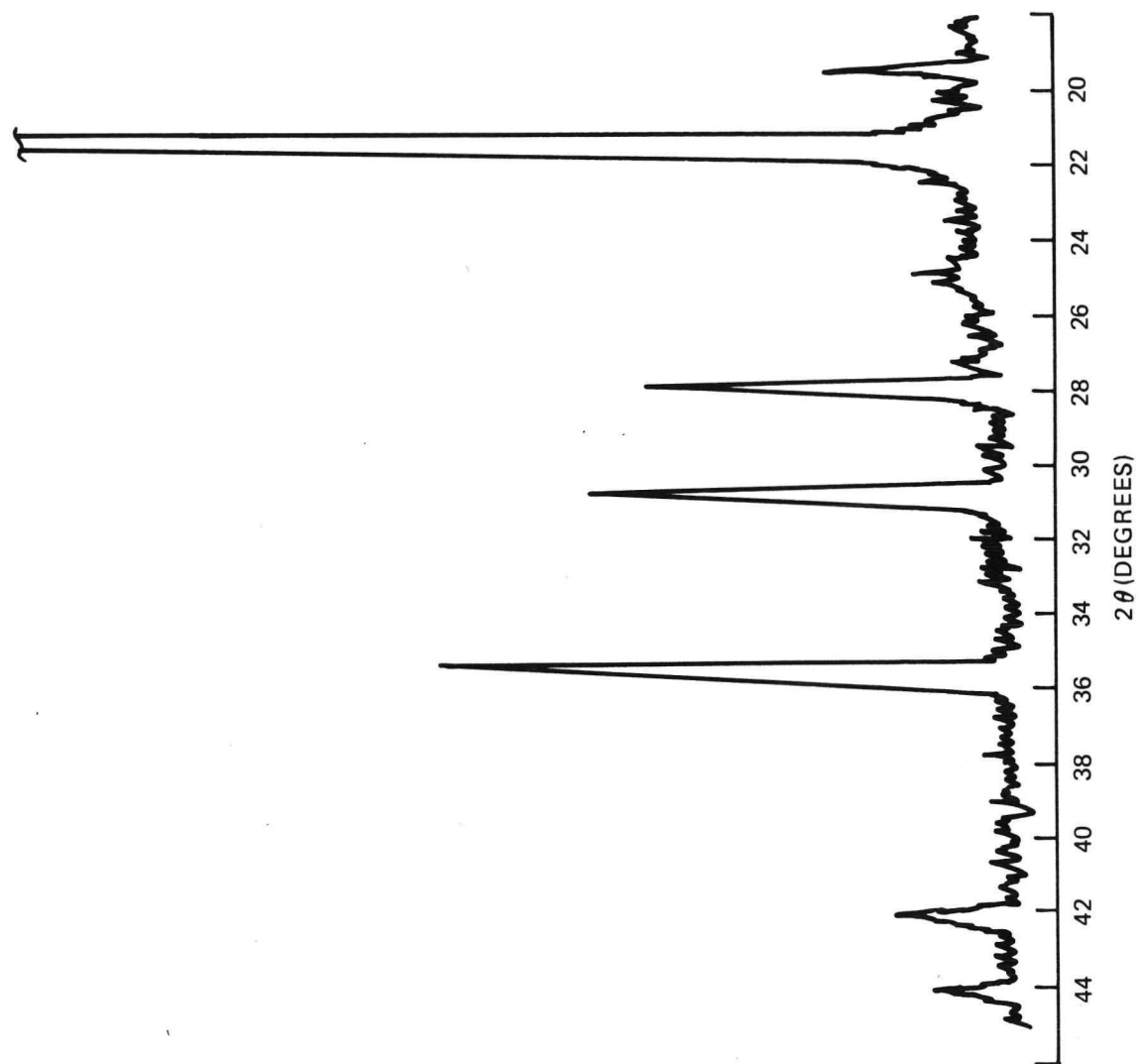


Figure 10. X-ray diffraction pattern for the unstabilized low (α) cristobalite phase of AlPO_4 . (Radiation: $\text{CuK}\alpha$)

2.4.2 THERMAL EXPANSION

Two techniques were used to prepare specimens for thermal expansion measurements. The first was to slurry the calcined fibers in distilled water and make a felt on a Buchner funnel. Since this method could tend to leach some soluble constituents from the fibers, a second technique was devised in which no water was used. The second method consisted of grinding the calcined fibers through a 200 mesh screen and dry pressing using a beeswax binder. Both types of bars were dried slowly at 322 K, 356 K, 394 K, 478 K, and 922 K for 1 hour at each temperature to assure complete removal of the water or binder. The dried specimens were fired in a closed vessel with a saturated BPO_4 atmosphere for 16 hours at 1561 K. Both specimens were stabilized with boron (Table 3, Composition 4).

The thermal expansion characteristics of each specimen are shown in Figure 11 up to 750° K. As anticipated from the x-ray diffraction data (which indicated that the high-cristobalite phase of AlPO_4 had been stabilized), the discontinuity in thermal expansion associated with the high-to-low cristobalite transformation has been eliminated. The thermal expansion level (although not as low as predicted) is approximately 1/2 that obtained for REI-Mullite. A logical extension of this work should establish the relationship between boron content and thermal expansion in this system.

2.4.3 MORPHOLOGY

Solutions spun (using the apparatus shown in Figure 4) yielded fibers having an average diameter of approximately 10 μm . A typical fiber-diameter distribution is shown in Figure 12. Minor changes in apparatus design and processing could produce fibers of smaller diameter; no attempt was made to produce smaller diameter fibers on this program.

Scanning electron photomicrographs of the boron-stabilized fibers (consolidated at two different temperatures) are shown in Figures 13 and 14. Some topographical changes were noted at the higher calcining temperature (i.e., increased grain-growth and decreased surface roughness). Figure 15 shows the boron-stabilized fibers in an RSI-type configuration. Rigidization was achieved through self-bonding of a water-felted mat. Thermal etching during fabrication indicated that a higher degree of grain growth occurred compared to the as-fabricated condition (Figure 14). This grain growth phenomenon was possibly catalyzed by water contamination during the felting operation. A more irregular fiber morphology resulted with the scandium-stabilized AlPO_4 system as shown in Figure 16.

2.4.4 THERMAL AGING

A series of post-fabrication aging studies were run on the boron-titanium stabilized fibers (Table 3, Composition 4) to determine if reversion to the low cristobalite form would occur. The fibers were placed in a platinum crucible and aged at 1533 and 1644 K

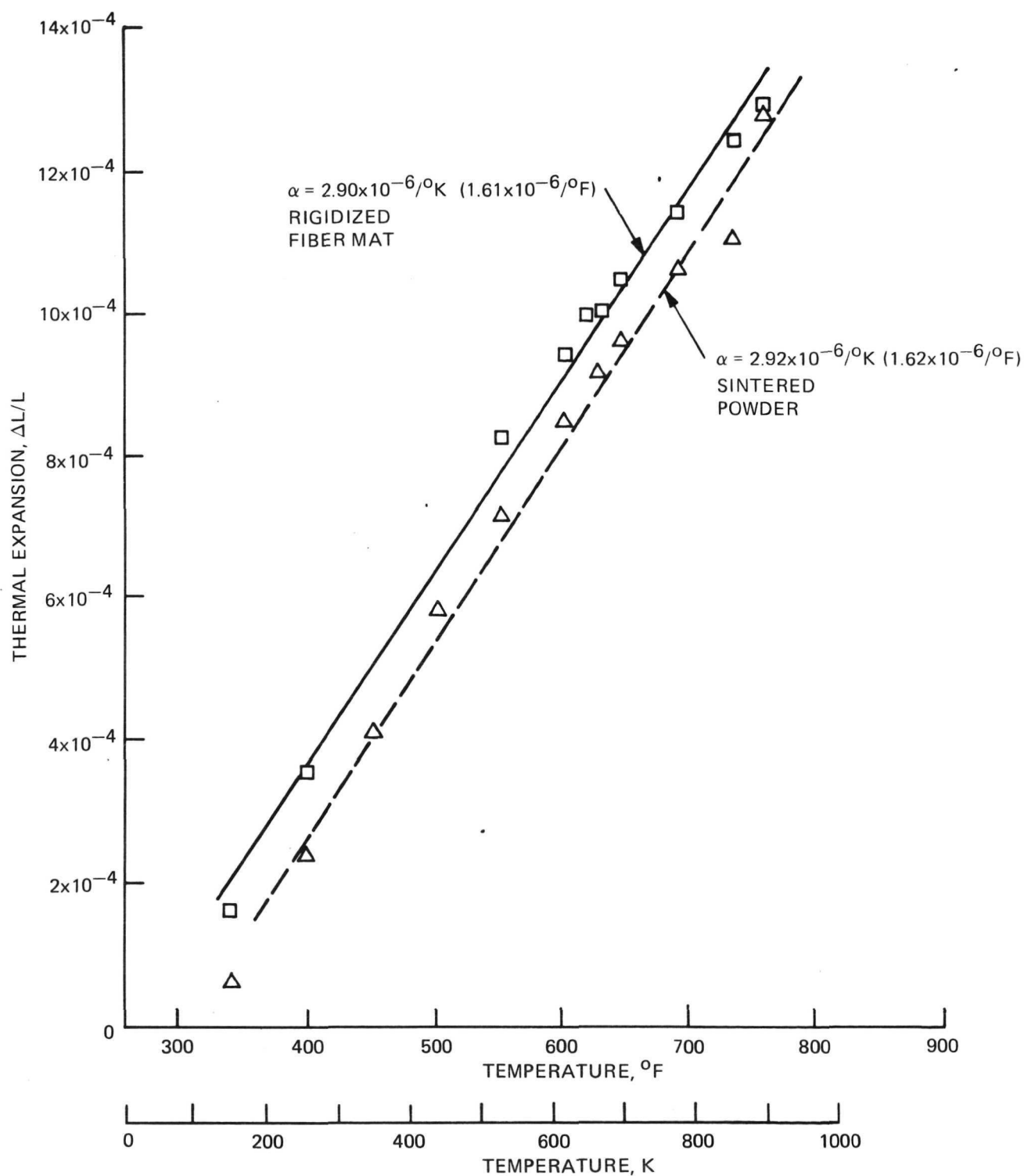


Figure 11. Thermal expansion of boron-stabilized AlPO_4 ($89 \text{ AlPO}_4\text{-}10\text{BPO}_4\text{-}1\text{TiO}_2$). Specimen configurations: RSI-type rigidized mat, cold-pressed and sintered pellet formed by grinding fibers into a powder.

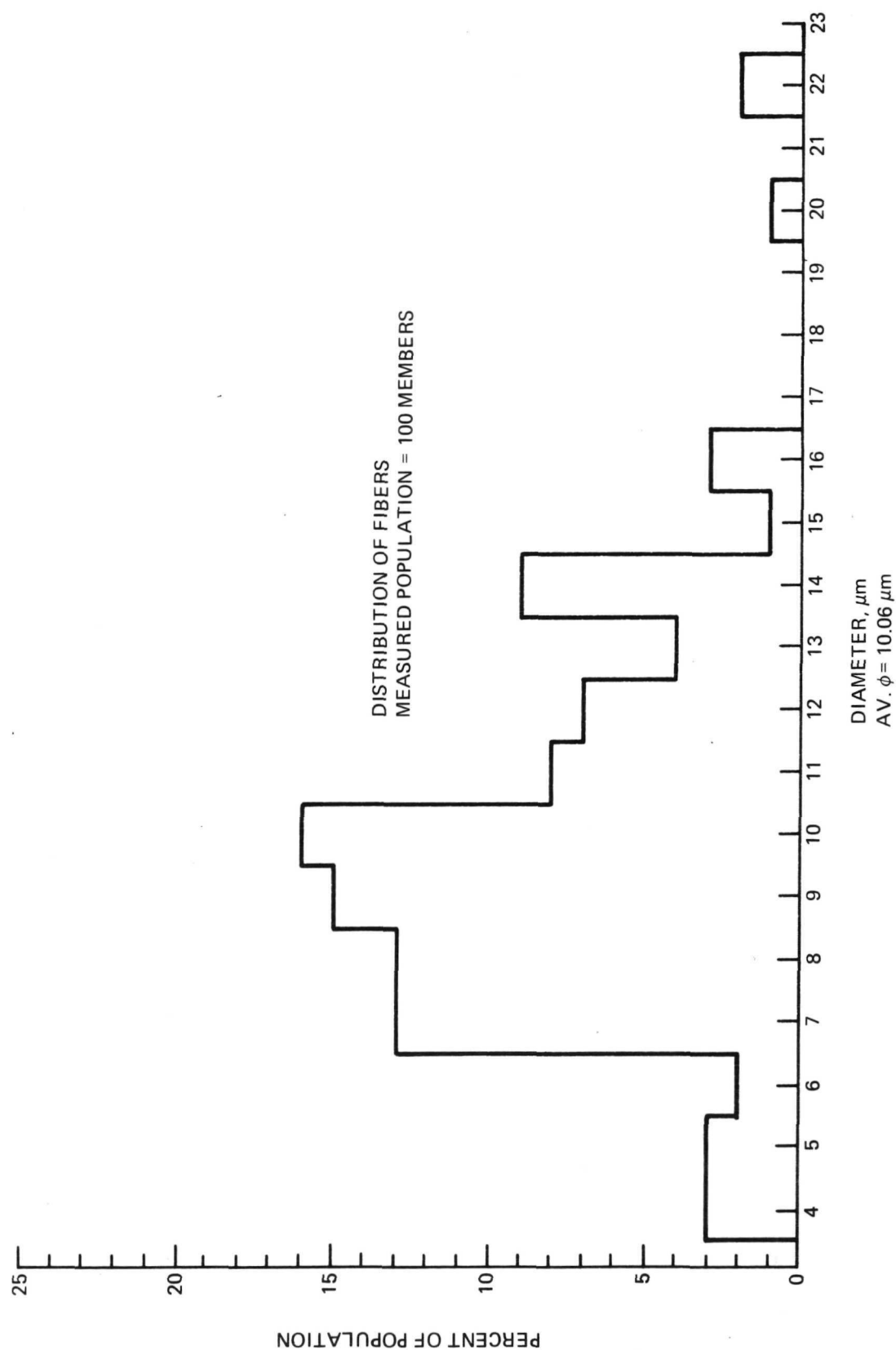
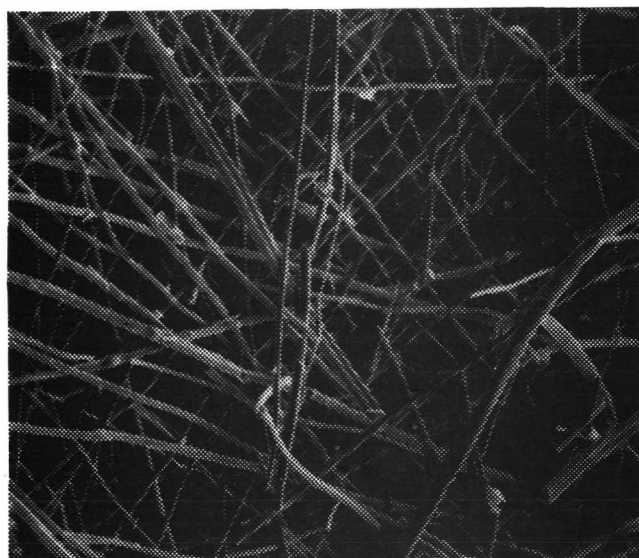
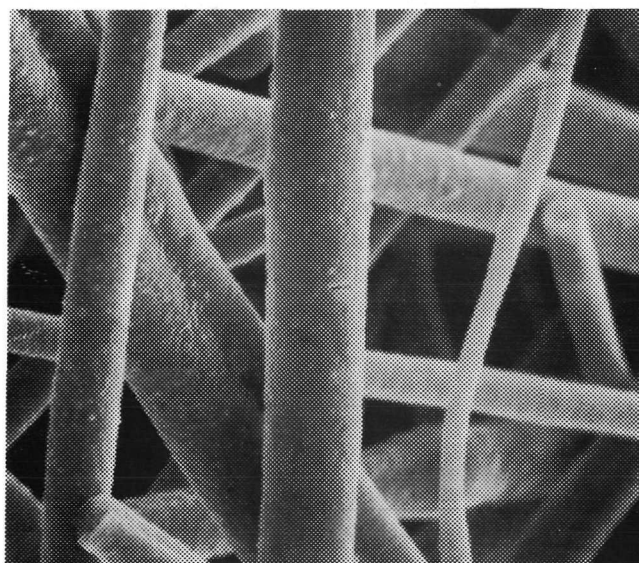


Figure 12. Typical fiber diameter distribution for boron-stabilized aluminum phosphate fibers

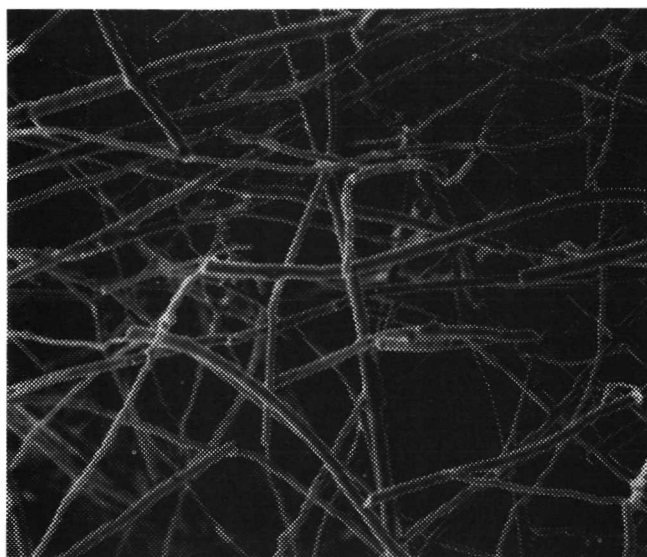


100 μm

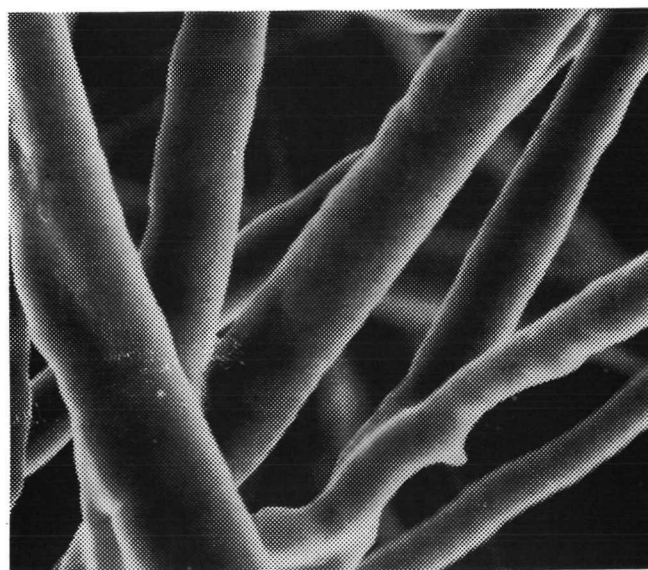


10 μm

Figure 13. SEM photographs showing the microstructure of boron-stabilized aluminum phosphate fibers ($89\text{AlPO}_4\text{-}10\text{BPO}_4\text{-}1\text{TiO}_2$). Heat treatment: 16 hrs. @ 1478 K (2200° F).

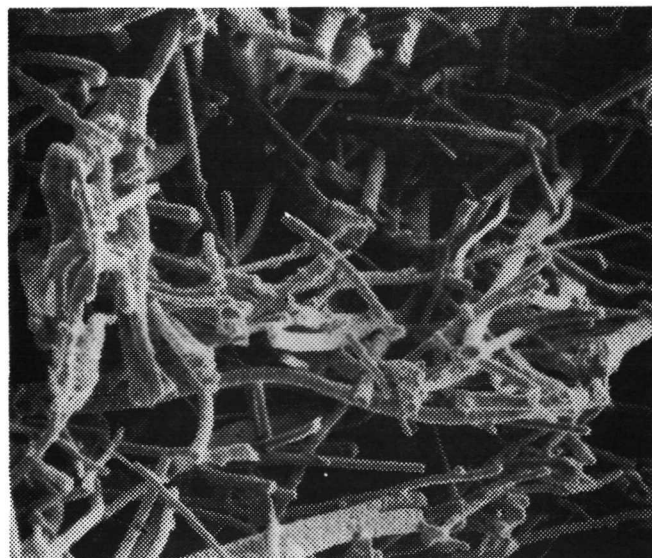


100 μm

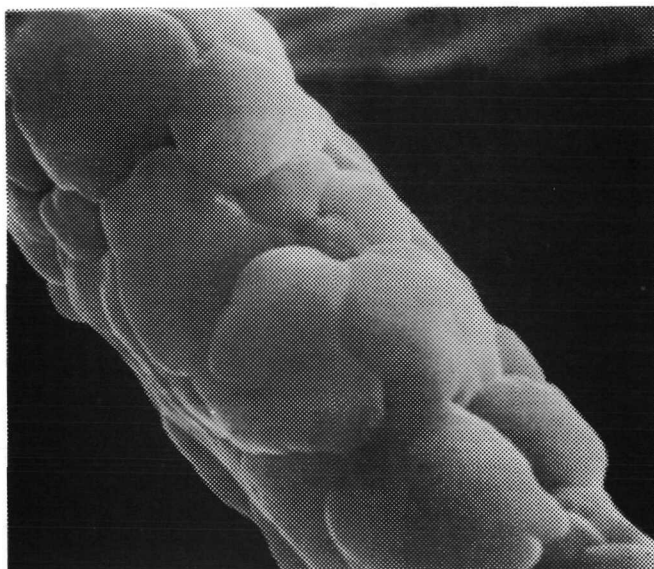


10 μm

Figure 14. SEM photographs showing the microstructure of boron-stabilized aluminum phosphate fibers ($89\text{AlPO}_4\text{-}10\text{BPO}_4\text{-}1\text{TiO}_2$). Heat treatment: 16 hrs. @ 1561 K (2350° F).

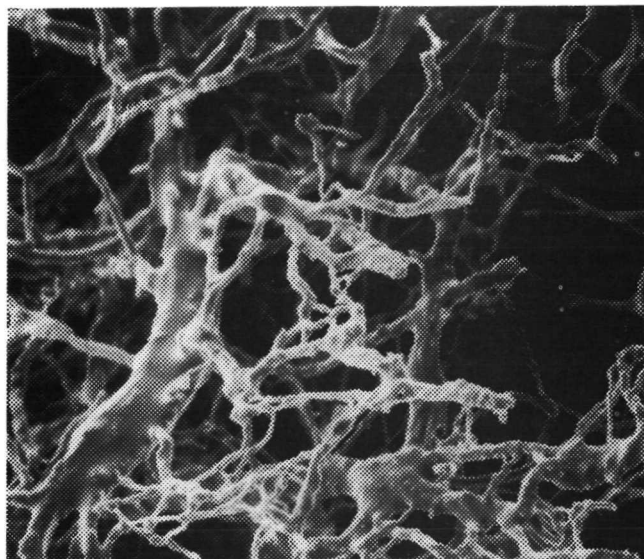


100 μm

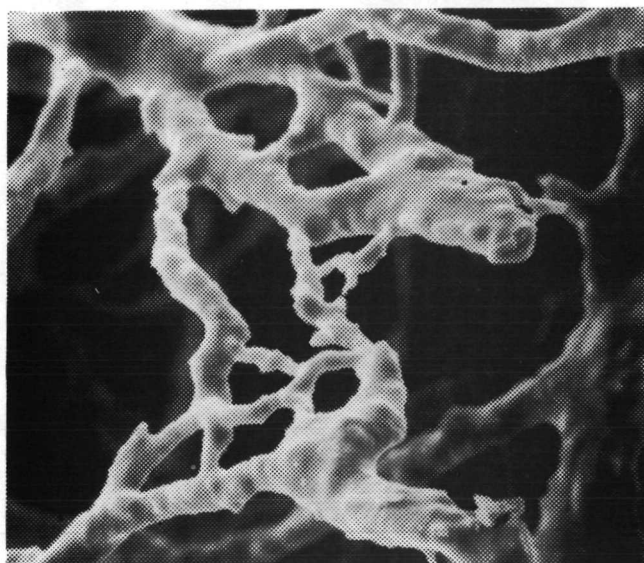


10 μm

Figure 15. SEM photographs showing the microstructure of boron-stabilized aluminum phosphate fibers ($89\text{AlPO}_4\text{-}10\text{BPO}_4\text{-}1\text{TiO}_2$) in a rigidized configuration. Fibers were water-felted into an RSI mat prior to calcining. Heat treatment: 16 hrs. @ 1561 K (2350° F).



100 μm



10 μm

Figure 16. SEM photographs showing the microstructure of scandium-stabilized aluminum phosphate fibers ($90\text{AlPO}_4-10\text{ScPO}_4$). Heat treatment: 16 hrs. @ 1533 K (2300° F).

for times ranging from one-half to sixteen hours. The x-ray diffraction patterns showed that this fiber composition reverted to 100% α -cristobalite almost immediately at temperatures above 1533° K.

Past experience with the multiphase Babcock and Wilcox mullite fiber has indicated that the P_2O_5 and B_2O_3 additives tend to vaporize when the fiber was heat treated in air above 1533 K (Reference 2). It is believed that the observed reversion was due to similar causes, however, confirming chemical analyses were not performed. Future studies of the boron-stabilized fiber, and also, the scandium-stabilized fiber (which was not evaluated for thermal stability on this program) should quantitatively assess the effect of stabilizer concentration on the observed reversion phenomena. Also, as observed on an earlier program, the role of specimen configuration on reversion kinetics should be determined. An indication of the possible effect of specimen configuration is described below.

A solid pellet was made by crushing calcined fibers of this same composition and mixing this with 20% by weight of P_2O_5 to promote sintering. This mixture was then pressed into a pellet using a beeswax binder and fired at 1561 K for 16 hours. The pellet, shown in Figure 17, was analyzed (XRD) and found to be 100% β -cristobalite. The pellet was then heat aged four (4) hours at 1644 K and re-analyzed. This sample showed only a very slight reversion to α -cristobalite showing that the bulk material with excess P_2O_5 was far more stable than the fibers. The relative effect of excess P_2O_5 and reduced surface area for vaporization (compared to a fibrous mat) on reversion kinetics remains to be determined.

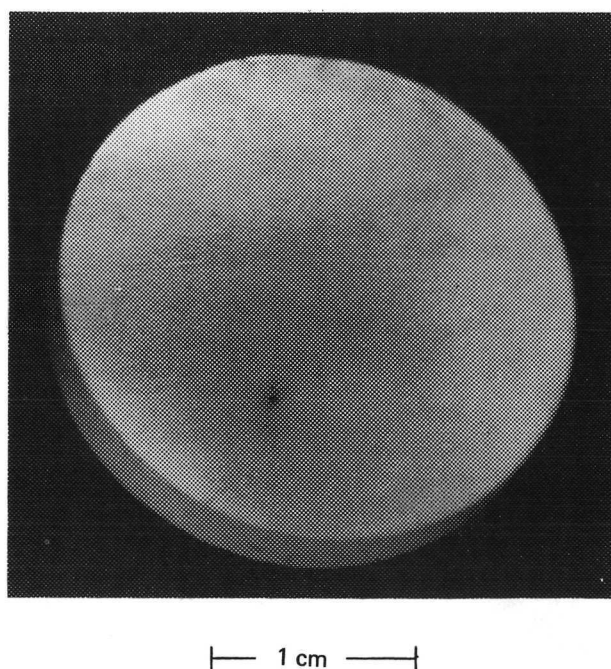


Figure 17. Solid-pellet of boron-stabilized $AlPO_4$ fabricated from crushed fibers (Table 3, Composition 4)

SECTION 3

DISCUSSION OF RESULTS

3.1 STABILIZER SELECTION

Of the several single-site substitutions attempted, successful stabilization was demonstrated with boron, boron and titanium, silicon and boron, and scandium. The lack of success at stabilization with the other substitutions attempted was not necessarily indicative of stabilizer unsuitability; but could be merely indicative of the unsuitability of the particular incorporation method and/or concentration level. This point is especially illustrated in the case of the boron stabilizer. In order to stabilize the high cristobalite phase of AlPO_4 it was necessary to carry-out the final homogenization step in a controlled atmosphere of BPO_4 vapor. Without this atmosphere, stabilization was not possible due to the vaporization of volatile constituent oxides (B_2O_3 , P_2O_5) prior to solid-solution formation.

Figure 18 compares the thermal expansion data for boron-stabilized AlPO_4 with unstabilized AlPO_4 and other ceramic oxide fibers evaluated as candidate RSI insulations for the Space Shuttle. The thermal expansion coefficient of the stabilized AlPO_4 at this stage of development was determined to be approximately 1/2 that of REI-Mullite, but still higher than REI-Silica by a factor of approximately 3. It is believed that further research with the boron-stabilized system (See Section 5.0) will result in thermal expansion levels approaching fused silica.

The apparent destabilization which occurred in a boron-stabilized RSI- AlPO_4 panel when subsequently aged in air (Section 2.4.4) could be a deterrent for its practical utilization, however, additional stabilization studies must first be conducted before this system is eliminated for RSI consideration.

For example, the effect of boron concentration on phase stability has yet to be evaluated. Also, the stability of multi-site simultaneous substitutions remains to be determined. Another consideration (from a systems performance viewpoint) is the apparent stability of coated REI-Mullite tiles (compared to uncoated tiles) in simulated Shuttle entry environments.

Although the scandium - stabilized fibers appeared to show better high temperature stability than the boron stabilized material, characterization studies concentrated on the boron-stabilized material for several reasons. For one thing, boron was far more practical from a cost standpoint; (high purity B_2O_3 is readily available for about \$5.50/kg compared to scandium chloride which is difficult to buy and costs about \$10,000/kg). Secondly the basic mechanical properties of the stabilized

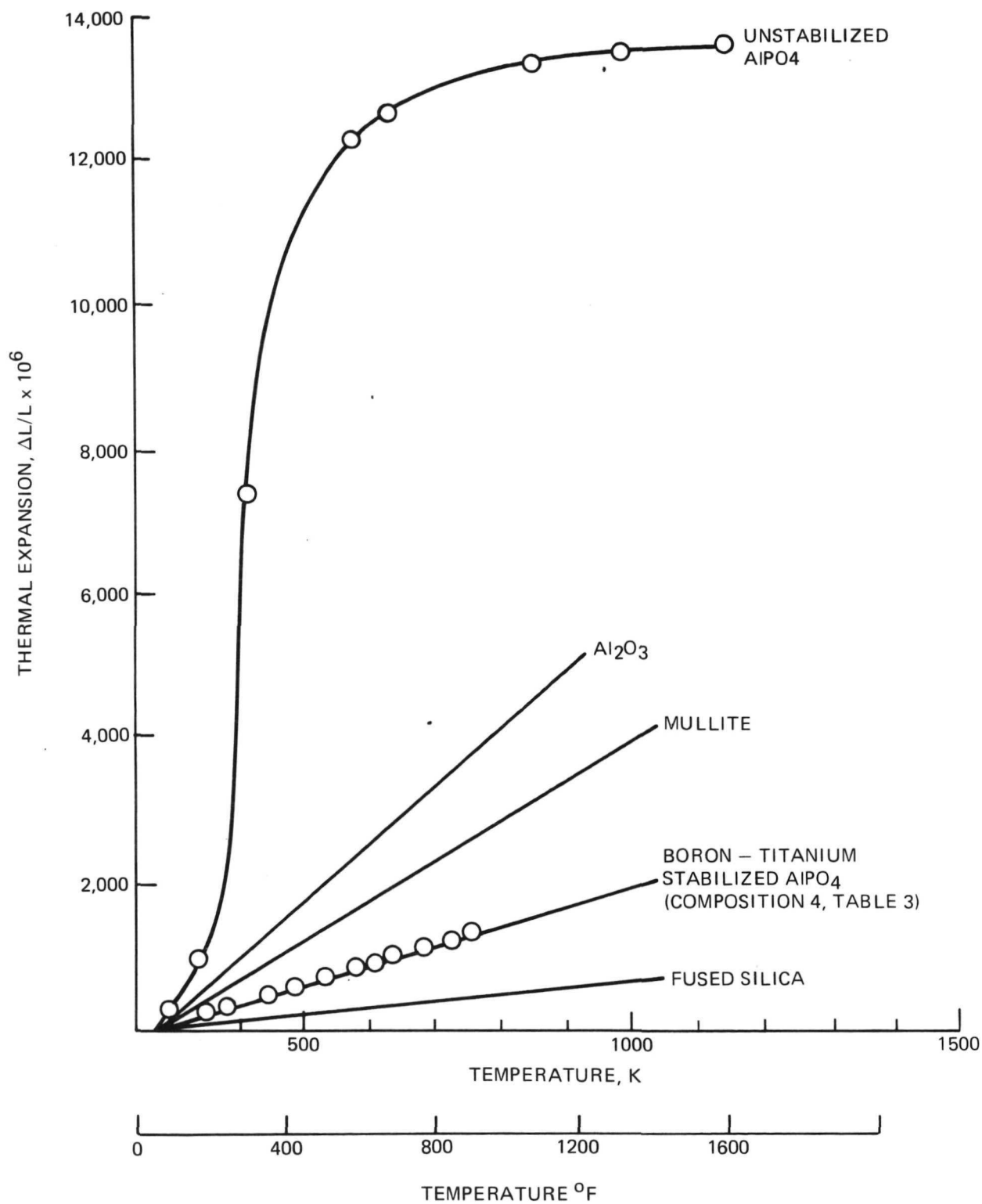


Figure 18. Comparison of thermal expansion characteristics of candidate RSI fibers.

material should be similar regardless of what stabilizers are used. Finally, the long lead-times and high-costs involved in obtaining sufficient quantities of ScCl_3 to run a characterization study of scandium stabilized fibers was impractical for the scope of this study.

3.2 FIBER SYNTHESIS

The salt-decomposition process (as applied to the formation of stabilized aluminum orthophosphate) has produced good-quality fibers. A patent disclosure letter (Reference 10) has been issued describing this process and patent-coverage is being pursued. Concurrently, a NASA-New Technology report has been submitted to NASA-Langley for evaluation.

Minor changes in processing equipment could result in the formation of smaller-diameter fibers (current process yields 10 μm fibers) and increased fiber yields. No attempt was made to evaluate and optimize these parameters on the current program.

SECTION 4

CONCLUSIONS

The AlPO_4 stabilization and fiber synthesis program led to the following conclusions:

1. The feasibility of stabilizing the high-cristobalite (β), low-expansion phase of AlPO_4 has been demonstrated. Stabilization was achieved with boron, combined boron and titanium, combined boron and silicon, and scandium substitutions.
2. A method for forming stabilized small-diameter AlPO_4 fibers (based upon the salt-decomposition technique) has been developed. A NASA "New Technology" report describing this innovation has been prepared.
3. Thermal expansion measurements on a boron: titanium, stabilized REI- AlPO_4 composite were approximately one-half ($1/2$) that measured previously on REI-Mullite.
4. The temperature level of phase-stability for scandium-stabilized AlPO_4 was considerably greater than boron, however, cost and material availability considerations detract from its practicality.
5. Stabilizer concentration and/or specimen configuration were found to effect reversion kinetics during post-fabrication thermal aging tests in air for the boron: titanium stabilized AlPO_4 fibers. (Table 3, composition 4)

SECTION 5

RECOMMENDATIONS FOR FUTURE WORK

1. It is recommended that research be continued to identify an optimum method for achieving a stabilized AlPO_4 fiber. Future work should evaluate stabilizer concentration as a variable as well as simultaneous substitutions at both the Al^{3+} and P^{5+} sites.
2. It is also recommended that fiber research be initiated to identify other low-expansion, refractory ceramic systems to complement the AlPO_4 research activity. Several candidate systems including other phosphates, tungstate- and vanadate-based solid solutions have already been identified by Hummel (References 11, 12, 13, and 14) and await experimental exploitation in fibrous form. Also, certain glass compositions in the SiO_2 : BPO_4 : B_2O_3 system have been identified which appear to be more resistant to devitrification than silica while retaining the many desirable attributes of silica. Fiber studies in this system appear fully warranted.

SECTION 6

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